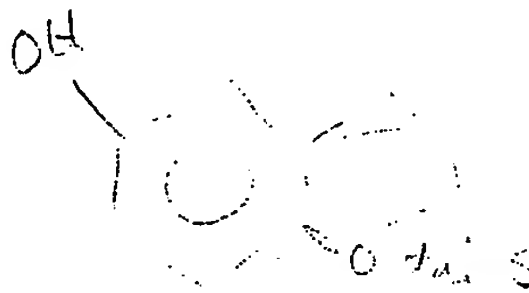


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O=C1OC2=CC=CC=C2O1

- Komogorov

- Polymeraantirakennetta stabilointi
kopolymeeri



- kypä polymeraatti
- missä haasto
- Massalissa kytös
- Alustaminen kemi-
- allistat polymeroin-
- aikana
- Polymeroituminen
- Wot. kolmas
- alustava
- josta splottak-
- ku

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Stabilizers for Plastic Materials

This invention relates to stabilizers for plastic materials, and more specifically, to stabilizing mixtures for improving the colour and processing stability of plastic materials.

Reducing oxidation and stabilizing the colour of polymers during
5 processing is important to the plastics industry. During processing into articles polymers are subjected to high temperatures and pressures which can have an adverse effect on the molecular weight and physical properties of the polymers and on the appearance of the finished articles made from these polymers. The need exists, therefore, for antioxidant and colour
10 stabilizing materials which minimize oxidation and colour instability.

United States Patent No. 4,806,580 discloses stabilizer mixtures for stabilizing plastic material, e.g. polyethylene or polypropylene, in processing. The disclosed stabilizer mixtures contain (a) a chroman derivative, e.g. dl- α -tocopherol, and (b) an organic phosphite or phosphonite in a
15 weight ratio (a:b) of 1:5 to 1:14.

Japanese Patent Publication (Kokai) No. 86036/1987 discloses stabilized polyolefin compositions, e.g. polypropylene, containing, per 100 parts by weight of the polyolefin, 0.005 to 0.5 parts by weight of a compound selected from the vitamin E group and 0.01 to 0.5 parts by weight of a bisaryl penta-
20 erythrityl diphosphite(I) or a triaryl phosphite(II).

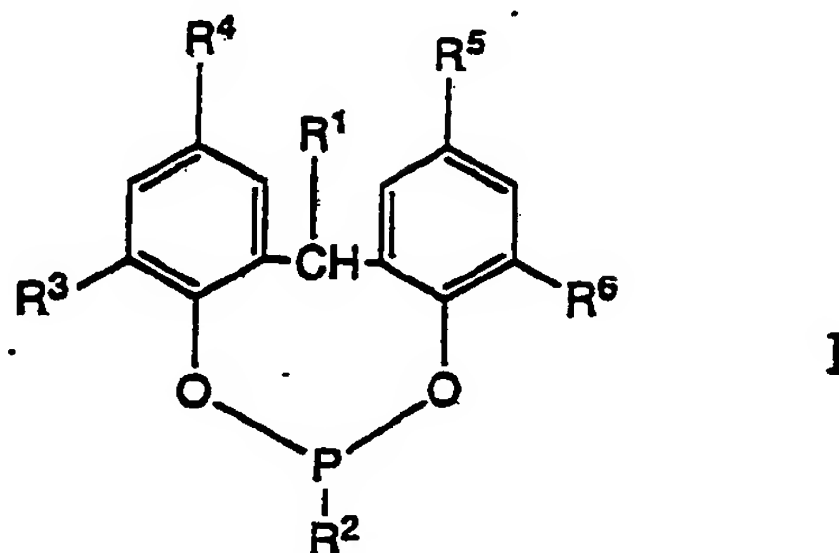
Japanese Patent Publication (Kokai) No. 55043/1979 discloses stabilized polyolefin compositions, e.g. polyethylene and polypropylene, containing a compound from the vitamin E group and various phosphites. In Examples 1-12 thereof the ratios of vitamin E:phosphite evaluated in polypropylene are
25 1:1.67 and 1:3.33.

It is an object of the present invention to provide stabilizer mixtures for plastic materials which contain polypropylene to improve the processing and colour stability.

Accordingly, the present invention provides stabilizing mixtures for
30 plastic materials containing polypropylene, comprising

(a) a tocopherol or other 6-chromanol compound

and (b) a phosphorus-containing secondary antioxidant of the general formula



wherein

5 R^1 signifies hydrogen or C_{1-6} -alkyl,

R^2 signifies halogen, C_{1-18} -alkyl, C_{1-18} -alkoxy or aryloxy

and

R^3 , R^4 , R^5 and R^6 , each independently, signify isopropyl or straight- or branched-chain C_{4-8} -alkyl,

10 wherein the weight ratio of component (a) to component (b) is from about 1:0.5 to about 1:20.

As used herein the term "tocopherol compound" refers to a compound having the basic tocopherol structure of the vitamin E group. Preferred tocopherol compounds for use as component (a) of the present stabilizing
15 mixtures are α -tocopherol and γ -tocopherol, particularly the first-mentioned tocopherol compound.

The term "other 6-chromanol compound", as also used herein in relation to the component (a) of the stabilizing mixtures of the present invention, indicates in particular substituted chroman-6-ols (in common
20 with the aforementioned "tocopherol compounds) featuring the same substitution patterns on their benzene moiety as α -, β -, γ - and δ -tocopherols and, at the 2-position, two methyl groups or a methyl and a hydroxymethyl group. Especially preferred such chroman-6-ols are 2-hydroxymethyl-2,5,7,8-tetramethylchroman-6-ol and 2,2,5,7,8-pentamethylchroman-6-ol.

25 As also used herein, the term "secondary antioxidant" refers to those compounds which are hydroperoxide decomposers, i.e. which have the ability to react with hydroperoxides to yield non-radical products, essentially decomposing hydroperoxides into stable by-products. Such compounds are the above-defined (phosphorus-containing) compounds of formula I. In the

pertinent definition, any alkyl group (as such or as part of "alkoxy") which contains at least 3 carbon atoms may be straight- or branched-chain, unless otherwise specified. Under the term "aryloxy" there is to be understood in particular phenoxy which is either unsubstituted or substituted with up to
5 three C₁₋₄-alkyl groups situated in the 2- and/or 4- and/or 6-position(s). The expression "halogen" embraces all four halogens, but preferably signifies fluorine. If R¹ signifies alkyl, this is preferably methyl. The alkyl substituents signified by R³, R⁴, R⁵ and R⁶ are preferably identical, even more preferably all tert.butyl. Particularly preferred compounds I for use as the
10 component (b) of the present stabilizing mixtures are 2,2'-ethylidene-bis(4,6-di-tert.butylphenyl) fluorophosphonite (available from Ethyl Corporation, U.S.A., under the trade name Ethanox® 398) and 2,2'-methylene-bis(4,6-di-tert.butylphenyl) octylphosphite (available from Argus Chemical Corp., Japan, under the trade name Mark HP-10).

15 The compounds of formula I are known or can be produced using methods known per se (see e.g. European Patent Publications 312790 and 357048).

The term "plastic material containing polypropylene" as used herein refers to those plastic materials which contain only polypropylene, i.e. homo-
20 polymers, copolymers which contain as one of the repeating units the polypropylene monomer moiety, or blends of polypropylene and one or more other polymers. Those skilled in the art will appreciate and will know how to make the different types of copolymers that can be formed with polypropylene, including alternating, block and graft copolymers as well as how
25 to make the blends of polypropylene with other polymers.

In the stabilizing mixtures of the present invention there may be present not only one tocopherol or other 6-chromanol compound (a) and one phosphorus-containing secondary antioxidant of formula I (b) but also, as desired, one or more further compounds (a) and/or (b). The definition of the
30 inventive stabilizing mixtures is always to be so interpreted, and in those cases where more than one tocopherol or other 6-chromanol compound and/or more than one phosphorus-containing secondary antioxidant are present the weight ratio 1:0.5 to 1:20 refers to total component (a) and/or (b).

The weight ratio of component (a) to component (b) is preferably from
35 1:1 to 1:10, even more preferably from 1:1 to 1:5, and most preferably about 1:4. A particularly preferred stabilizing mixture for plastic materials

according to the present invention consists essentially of α -tocopherol as the component (a) and 2,2'-ethyldene-bis(4,6-di-tert.butylphenyl) fluorophosphonite as the component (b) in a weight ratio (a):(b) of about 1:4.

The stabilizing mixtures of the present invention may be produced by simple physical mixing of the components (a) and (b) with each other in the desired weight ratio. Preferably an intimate, homogeneous mixture of the two components is thereby achieved. The methods of admixture and the equipment used for this purpose are well known to the person skilled in the art. The physical mixing process represents a further aspect of the present invention.

The stabilizing mixtures of the present invention featuring the ratio of (a):(b) of from about 1:0.5 to about 1:20 by weight produce improved processing stability and colour stability, while maintaining the heat aging stability, for the polypropylene-containing-plastic materials incorporating such mixtures.

The methods of incorporating the stabilizing mixtures of the present invention into the plastic materials to be stabilized thereby may be effected by the conventional methods which are generally utilized for the stabilization of plastic materials by additives. These methods are well known per se by persons skilled in the pertinent art and may involve the incorporation of the stabilizing mixture as such or of the components (a) and (b) individually, in the correct ratio, at any convenient stage of the manufacture or processing of the plastic material. In one embodiment, a small portion of the total stabilizing mixture is added immediately after the polymerization itself, just before the subsequent drying stage, and the rest is incorporated during the pelletizing stage.

In each case the stabilizing mixture according to the present invention is generally incorporated in a concentration of from about 0.005 to about 1%, preferably from 0.02 to 0.125%, by weight, based on the total weight of the components (a) and (b) in relation to the weight of the plastic material to be stabilized.

The present invention comprises as a further aspect plastic materials containing polypropylene, and articles manufactured therefrom, characterized in that they have been stabilized by incorporation therein of a stabilizing mixture in accordance with the present invention and as defined

hereinabove. Moreover, the use of these stabilizing mixtures for stabilizing plastic material containing polypropylene also represents a further aspect of the present invention.

In addition to the above-defined stabilizing mixtures, further new formulations containing as one component α -tocopherol have now been found to possess stabilizing properties for plastic materials. These stabilizing formulations, as also provided by the present invention, comprise (a) α -tocopherol and (b) one or more polyhydroxy compounds, wherein the weight ratio of component (a) to component (b) is from about 1:0.5 to about 1:4.

These stabilizing formulations may be produced by simple physical mixing of the two components (a) and (b) with each other in the desired weight ratio, preferably in such a way as to achieve an intimate, homogeneous mixture. In some cases the stabilizing formulations are clear solutions, which remain so even after being frozen and then thawed. The intimate mixing of the components is then suitably carried out by stirring together in suitable equipment, until a clear solution results. In general the stabilizing formulations are particularly effective in stabilizing the plastic material in which they are incorporated against undesired discolouration, especially yellowing, during processing.

As used in this aspect of the present invention the term "polyhydroxy compound" embraces any compound featuring at least two hydroxyl groups. Preferred such compounds are ethylene glycol, butylene glycol, glycerol, trimethylolpropane, pentaerythritol, triisopropanolamine, panthenol, boric acid, glyceryl monostearate and glyceryl(mono)caprylate/caprate.

In relation to the above-described stabilizing formulations the term "plastic material" embraces not only the "plastic materials containing polypropylene" as described hereinabove but also plastic materials, including thermoplastic materials, which include other types of polymers, such as polyethylene, polyvinyl chloride, polystyrenes and polyurethanes. Accordingly, these plastic materials are not limited to those containing polypropylene, or even to polyolefines. Blends of two or more different types of polymers or copolymers are naturally included in the "plastic materials" to be stabilized by the present stabilizing formulations. Preferably the plastic materials stabilized by the stabilizing formulations of the present invention are plastic materials containing polypropylene.

Preferably, these stabilizing formulations feature a weight ratio of component (a) to component (b) of from 1:1 to 1:2, even more preferably of about 1:2. The stabilizing formulations may contain, in addition to the aforementioned components (a) and (b), other additives to facilitate their preparation by mixing, e.g. emulsifying agents. A particularly preferred emulsifying agent for this purpose is glyceryl(mono)caprylate/caprate, available from Drew Chemical Co. under the trade name Drewmulse® GMC-8. This may be used as the sole emulsifying agent or, if desired, in combination with one or more other suitable ingredients in an emulsifying system. A particularly preferred emulsifying system consists of glyceryl(mono)caprylate/caprate in combination with polyethylene glycol.

A particular class of the above stabilizing formulations consists of those comprising (a) α -tocopherol and (b) one or more polyhydroxy compounds, wherein the weight ratio of component (a) to component (b) is from about 1:0.5 to about 1:4, with the exclusion of a stabilizing formulation comprising

(c) from about 10 to about 50 percent by weight of α -tocopherol;

(d) up to 50 percent by weight of polyethylene glycol and/or

(e) up to 50 percent by weight of glyceryl(mono)caprylate/caprate;

and optionally also (f) up to 20 percent by weight of glycerol,

whereby the total percent by weight of the two, three and four components (c) to (f), as appropriate, amounts to 100.

The present invention embraces the above-indicated process for producing these formulations, comprising, more particularly, mixing in the desired weight ratio the above-defined components (a) and (b) with each other, in appropriate cases until a clear solution is formed. If any other components, e.g. an emulsifying agent such as the aforementioned glycerol monocaprylate caprate, are to be present in the finished formulation these can be mixed with the components (a) and (b) simultaneously. Specific methods and equipment for the mixing process are well known to the person skilled in the art.

As in the case of the aforementioned "stabilizing mixtures for plastic materials containing polypropylene" the present stabilizing formulations also improve the processing stability and colour stability, while maintaining the heat aging stability, of the plastic materials in which they are

incorporated, particularly the colour stability. Furthermore, the methods of incorporating these stabilizing formulations into the plastic materials to be stabilized thereby may in this case too be effected by conventional methods which are generally utilized for the stabilization of plastic materials by additives and which are well known by persons skilled in the pertinent art. In each case the stabilizing formulation is generally incorporated in a concentration of from about 0.01 to about 1% by weight, based on the total weight of the components (a) and (b) in relation to the weight of the plastic material to be stabilized, preferably in a concentration of 0.05 to 0.25% by weight. It has been found that these stabilizing formulations are readily incorporated at low concentrations and become well dispersed in the plastic material in which they are incorporated.

The present invention comprises as further aspects plastic materials, and articles manufactured therefrom, characterized in that they have been stabilized by incorporation therein of a stabilizing formulation according to the present invention and as defined hereinbefore, and the use of these stabilizing formulations for stabilizing such plastic materials.

In addition to the above-defined stabilizing mixtures comprising a tocopherol or other 6-chromanol compound and a phosphorus-containing secondary antioxidant of formula I and stabilizing formulations comprising α -tocopherol and a polyhydroxy compound, certain combinations of α -tocopherol, a phosphorus-containing secondary antioxidant of the above-defined formula I and a polyhydroxy compound have also been found to possess valuable stabilizing properties for plastic materials containing polypropylene. Accordingly, the present invention comprises as a further aspect a stabilizing three-component mixture for plastic materials containing polypropylene comprising

(a) from about 4 to about 50 percent by weight of α -tocopherol,

(b) from about 4 to about 70 percent by weight of a phosphorus-containing secondary antioxidant of the general formula I, as defined hereinabove,

and (c) from about 4 to about 70 percent by weight of a polyhydroxy compound,

whereby the total percent by weight of the three components (a), (b) and (c) amounts to 100.

The same preferences apply in respect of the phosphorus-containing secondary antioxidant and of the polyhydroxy compound as indicated
5 hereinabove for these components of the stabilizing mixtures and the stabilizing formulations, respectively, of the present invention.

As used in the above definition the term "polyhydroxy compound" is to be interpreted in accordance with the previous definition pertaining to the stabilizing formulations of the present invention. Furthermore, there may be
10 present not only one phosphorus-containing secondary antioxidant of formula I (b) and one polyhydroxy compound (c) but also, as desired, one or more further compounds (b) and/or (c). The definition of the inventive stabilizing three-component mixtures is always to be so interpreted, and in those cases where more than one phosphorus-containing secondary anti-
15 oxidant of formula I and/or polyhydroxy compound are present the given percentage weight ranges for components (b) and (c) refer to total component (b) and/or (c). The term "plastic material containing polypropylene" is to be interpreted as indicated hereinabove for the stabilizing mixtures of the present invention which comprise a tocopherol or other 6-chromanol
20 compound and a phosphorus-containing secondary antioxidant of formula I.

As in the case of the aforementioned "stabilizing mixtures for plastics materials containing polypropylene" the present stabilizing three-component mixtures also improve the processing stability, colour stability and heat aging stability of the plastic materials in which they are
25 incorporated. The methods of producing these stabilizing mixtures and of incorporating them into the plastic materials to be stabilized thereby may in this case too be effected by conventional mixing and incorporation methods well known by persons skilled in the pertinent art. In each case the stabilizing formulation is generally incorporated in a concentration of from
30 about 0.01 to about 0.25% by weight, based on the weight of the plastic material to be stabilized. The incorporation may also involve adding conventional additives, such as emulsifying agents, to facilitate the mixing.

The present invention comprises as further aspects plastic materials containing polypropylene, and articles manufactured therefrom,
35 characterized in that they have been stabilized by incorporation therein of a stabilizing three component mixture according to the present invention and

as defined hereinbefore, and the use of these stabilizing mixtures for stabilizing such plastic materials.

The technique of γ -irradiation of polymers, e.g. plastic materials containing polypropylene in order to effect material property changes is known [see e.g. H. Wilski, Prog. Coll. Polym. Sci. 58, 77 (1975), L.Wuckel et al., Isotopenpraxis 8, 1 (1972), H. Wilski, Kunststoffe 58, 18 (1968) and H.Fischer et al., Kunststoffe 58, 625 (1968)]. It is used inter alia for the sterilization of polymers used in the packaging of foodstuffs and of polymers in various medical applications. In a recent communication by D.W.Allen et al. in Chemistry & Industry (19.8.92, page 580) the authors report the effects of γ - and electron-beam irradiation on α -tocopherol used to stabilize polypropylene and concludes that α -tocopherol is far more easily transformed during such irradiation than other hindered phenol antioxidants such as Irganox® 1076 [octadecyl 3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate] and Irganox® 1010 [pentaerythritol tetrakis-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate], and that based on the level of γ - or electron beam-irradiation usually applied in such irradiation treatments it is unlikely that α -tocopherol will play a significant role as an antioxidant in food-contact polymers intended for use in food irradiation applications.

It has now been found that when α -tocopherol and other tocopherols and 6-chromanol compounds are used in combination with the phosphorus-containing secondary antioxidants of the above formula I, or with polyhydroxy compounds in the case of α -tocopherol, or with such phosphorus-containing secondary antioxidants and polyhydroxy compounds, again in the case of α -tocopherol, then such stabilizing mixtures are significantly better stabilizers than α -tocopherol, or other tocopherols and 6-chromanol compounds, as appropriate, used alone in plastic materials containing polypropylene when such stabilized plastic materials are subjected to γ -irradiation at a particular dosage. Accordingly, the present invention also provides the above-defined stabilized plastic materials containing polypropylene, and articles manufactured therefrom, whenever subjected to γ -irradiation at a dose of from about 0.5 to about 5.0 Mrad (such as is effected utilizing cobalt-60 as the source of γ -irradiation).

The following examples illustrate the present invention in its various aspects.

Example 1

Unstabilized polypropylene homopolymers, as powders (the "base powders"), were obtained from ICI (Chemicals and Polymers), Wilton, UK and are identified below as ICI-B, ICI-H and ICI-K. They were stored at low ambient temperature in a dark, unheated room.

Catalyst residues in these base powders were measured by plasma emission spectroscopy (Ti, Al) and a bomb method (Cl), the approximate values found being: titanium, 25 ppm; aluminium, 30 ppm; and chlorine, 25 ppm.

The melt flow index (MFI) of the base powders were measured at 190°C/10 kg using the method BS (British Standard) 2782 Part 7 method 720A, which is equivalent to ASTM (American Society for Testing and Materials: American National Standard) D1288, Condition N. Values were 18 for ICI-B, 28 for ICI-H and 24 for ICI-K, in each case being measured in the presence of 1% Irganox® 1010 [pentaerythritol tetrakis-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate; available from Ciba-Geigy] as stabilizer. The 230°C/2.16 kg values (ASTM D1238 condition L) are estimated approximately as 1.1, 1.7 and 1.5 for ICI-B, ICI-H and ICI-K, respectively.

Stabilizers in powder form and masterbatches were blended into the appropriate amount of ICI-B, ICI-H or ICI-K powder using a Pascall Lab-Mixer II mixer, at about 23 rpm with a cycle time of about 5 minutes.

Where stabilizers were in liquid form, for example, α -tocopherol and several polyhydroxy compounds, masterbatches in the concentration range 0.5 - 5% w/w, as appropriate, were first made by dissolving the liquid additive in a suitable organic solvent, for example, methanol or dichloromethane, and mixing the solution well into a few hundred grams of ICI-B, ICI-H or ICI-K powder. The solvent was then removed by rotary evaporation at reduced pressure. The resulting materials were then blended into an appropriate amount of ICI-B, ICI-H or ICI-K powder using the Pascall Lab-Mixer II under the conditions indicated above. Persons skilled in the art will also recognize that commercially available equipment for direct injection of liquid additives into extruders is also suitable for the incorporation of the stabilizer mixtures into the polypropylene.

The extruder residence times had previously been established by "starve feeding"; to minimize cross-contamination from the previous batch, the hopper was allowed to run out until the screw flights were exposed before the new powder blend was added. In each case the first 200 g of extrudate was
 5 rejected. After the extruder had reached equilibrium and a standard batch of polypropylene had been used to purge out the screw, batches were sequentially extruded. Unless otherwise stated, extrusion was carried out in air.

Melts were extruded through a 6 mm rod die, the lace fed into a water
 10 bath, through a haul off and air knife (to remove surface water) and granulated either in-line or collected and separately granulated later.

Extrusion was effected on a twin screw Brabender machine with counter-rotating screws, 30 mm diameter barrel and a L/D (length/dia-
 15 meter) ratio of 16:1. This extrusion was primarily for obtaining efficient blending of the additives with relatively little mechanical work being done on the polymer. The approximate running conditions were as follows:

-----Temperatures (°C)-----					Screw speed	Output
Hopper	zone 2	zone 3	die	melt	(rpm)	(kg/h)
220	225	230	235	230	15	7.5

During these runs, the instantaneous outputs were measured by weighing timed samples, referred to as first pass, and retained for
 20 colour/MFI measurements and oven aging.

Subsequent extrusions for assessment of MFI change during regranulation were effected on a Brabender single screw extruder with 30 mm diameter, compression ratio 3:1 and configuration L/D 20:1. For reextrusion, the melt temperature chosen was substantially higher, being
 25 approximately 270°C, in order to show more clearly the different effectivenesses of the various systems. The approximate running conditions were as follows:

-----Temperatures (°C)-----					Screw speed	Output
Hopper	zone 2	zone 3	die	melt	(rpm)	(kg/h)
265	270	275	280	270	100	3.5

The first single screw pass (second overall pass) was granulated, the product (less 200 g as previously discussed) refed into the hopper and this
 5 procedure repeated twice more to obtain a sample that had been extruded a total of four times.

Colour and MFI were determined on granules from both first and fourth extrusion passes.

The colour values were measured on granules in enclosed cells on
 10 Minolta or Dr. Lange instruments using illuminant C or illuminant D65, respectively. The machine outputs, respectively Yxy and CIE (Commission Internationale de L'Eclairage) L*a*b*, were averages and the means converted to ASTM D1925 yellowness index (YI) values.

MFI was measured at 230°C/2.16 kg (BS 2782 Part 7 method 720A,
 15 equivalent to ASTM D1238 condition L). The lowest granule MFI was also remeasured at 190°C/10 kg, from which estimates of powder MFI at 230°C/2.16 kg could be obtained.

Oven aging of the formulations was determined as follows:

Compression moulded plaques were obtained at 190°C; 30 g/170 g
 20 samples were used to press nominally 0.5 mm/3.0 mm thick mouldings respectively. In each case, a strip 1 cm wide was removed from the outside to avoid any contamination. Oven aging was determined on 5 cm square sections.

Oven aging was carried out in Gallenkamp OV330 size 2 circulating air
 25 ovens where temperature control was accurate to +/-1°C. Measurements were carried out at 150°C, 135°C and 120°C on duplicate samples arranged horizontally on stainless steel mesh trays. Initial signs of powdering were recorded, but in each case the embrittlement point was taken when a sample

flexed manually through 180°C became brittle. Results were recorded using hour meters, with the average time in days for two samples taken as the embrittlement time.

The data appear in Tables 1 to 6 hereinafter.

Table 1: Stabilization of Polypropylene (ICI-H) with Tocopherol/6-Chromanol (a) + P-containing sec. Antioxidant I (b)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a):(b) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)			Yellowness Index (YI) at Pass (Ps)			Oven Aging, Days to Embrittlement		
		1st Ps	4th Ps	%increase	1st Ps	4th Ps	150°C	135°C	120°C	
None (unstabilized)	- (comparative)	8.3	96.0	1056.63	6.0	13.7	1	1	1	
ATP ¹⁾ (100)	- (comparative)	5.8	14.0	141.38	10.7	17.5	1	3	9	
ATP (250)	- (comparative)	4.7	9.1	93.62	13.6	21.4	1	4	13	
ATP (250) + E 398 ²⁾ (250)	1:1 (500)	5.2	10.0	92.31	8.4	16.9	1	3	11	
ATP (250) + E 398 (500)	1:2 (750)	4.6	10.0	117.39	8.5	16.2	1	4	12	
ATP (250) + E 398 (1000)	1:4 (1250)	4.8	8.5	77.08	7.9	16.0	1	4	13	

Table 1: Stabilization of Polypropylene (ICI-H) with Tocopherol/6-Chromanol (a) + P-containing sec. Antioxidant I (b)
(continued)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a):(b) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)			Yellowness Index (YI) at Pass (Ps)		Oven Aging. Days to Embrittlement		
		1st Ps	4th Ps	%increase	1st Ps	4th Ps	150°C	135°C	120°C
ATP (250) + E 398 (2250)	1:9 (2500)	4.2	8.8	109.52	9.7	18.4	1	5	14
ATP (250) + TNPP3 (250)	- (comparative)	5.6	11.0	96.43	13.7	20.5	1	4	13
ATP (250) + TNPP (500)	- (comparative)	5.7	11.0	92.98	17.3	23.0	1	4	12
ATP (250) + TNPP (1000)	- (comparative)	5.7	12.0	110.53	17.2	23.5	1	4	11
ATP (250) + TNPP (2250)	- (comparative)	5.9	13.0	120.34	15.8	24.1	1	4	12

Table 1: Stabilization of Polypropylene (ICI-H) with Tocopherol/6-Chromanol (a) + P-containing sec. Antioxidant I (b)
(continued)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a):(b) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)			Yellowness Index (YI) at Pass (Ps)		Oven Aging. Days to Embrittlement		
		1st Ps	4th Ps	%increase	1st Ps	4th Ps	150°C	135°C	120°C
GTP4) (250) + E 398 (1000)	1:4 (1250)	4.3	10.0	132.56	11.6	18.5	1	5	16
GTP (250)	- (comparative)	4.9	11.0	124.49	16.0	24.2	1	5	13
GTP (250) + TNPP (1000)	- (comparative)	5.0	12.0	140.00	17.5	27.3	1	5	16

Table 2: Stabilization of Polypropylene (ICI-B) with Tocopherol/6-Chromanol (a) + P-containing sec. Antioxidant I (b)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a):(b) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)			Yellowness Index (YI) at Pass (P)	
		1st Ps	4th Ps	%increase	1st Ps	4th Ps
ATP (250)	- (comparative)	1.3	5.3	307.69	3.5	10.7
ATP (250) + E 398 (1000)	1:4 (1250)	1.1	2.7	145.45	2.2	9.0
ATP (250) + TNPP (1000)	- (comparative)	1.8	3.7	105.56	3.5	10.0

Table 3: Stabilization of Polypropylene (ICI-B) with Tocopherol/6-Chromanol (a) + P-containing sec. Antioxidant I (b)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a) : (b) (Total ppm)	Oven Aging: Days to Embrittlement			
		3 mm thick		0.5 mm thick	
		150°C	135°C	135°C	120°C
ATP (250)	-	1	7	4	14
ATP (250) + E 398 (1000)	(comparative) 1:4 (1250)	2	7	4	13
ATP (250) + TNPP (1000)	(comparative)	2	8	4	14

Table 4: Stabilization of Polypropylene (ICI-K) with Tocopherol/6-Chromanol (a) + P-containing sec. Antioxidant I (b)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a):(b) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)			Yellowness Index (YI) at Pass (Ps)	
		1st Ps	4th Ps	%increase	1st Ps	4th Ps
None (unstabilized)	- (comparative)	8.6	28	225.58	-1.7	3.6
ATP (250)	- (comparative)	5.0	8.5	70.00	4.5	12.4
ATP (250) + E 398 (1000)	1:4 (1250)	4.2	6.2	47.62	2.7	13
ATP (250) + HP-10 ⁵ (1000)	1:4 (1250)	4.0	5.1	27.50	1.3	7.5
ATP (250) + TNPP (1000)	- (comparative)	5.5	14.1	156.36	9.8	16.3
ATP (100) + E 398 (400)	1:4 (500)	6.2	12.6	103.23	-0.9	1.3

Table 4: Stabilization of Polypropylene (ICI-K) with Tocopherol/6-Chromanol (a) + P-containing sec. Antioxidant I (b)
(continued)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a):(b) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)			Yellowness Index (YI) at Pass (Ps)	
		1st Ps	4th Ps	%increase	1st Ps	4th Ps
ATP (250) + E 398 (250)	1:1 (500)	5.3	9.5	79.25	1.7	8.4
ATP (100) + HP-10 (400)	1:4 (500)	4.8	10.3	114.58	0.5	6.8
ATP (250) + HP-10 (250)	1:1 (500)	4.9	10.5	114.29	2.8	10.3
GTP (250) + E 398 (1000)	1:4 (1250)	3.7	6.6	78.38	5.8	17.7
E 16 (250) + E 398 (1000)	1:4 (1250)	3.8	5.6	47.37	5.2	15.8

Table 4: Stabilization of Polypropylene (ICI-K) with Tocopherol/6-Chromanol (a) + P-containing sec. Antioxidant I (b)
(continued)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a):(b) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)			Yellowness Index (YI) at Pass (Ps)	
		1st Ps	4th Ps	%increase	1st Ps	4th Ps
HMC ⁷⁾ (250) + E 398 (1000)	1:4 (1250)	4.0	5.8	45.00	10.1	20.3
ATP (250) + E 398 (1000) + GMC-8 ⁸⁾ (250)	1:4 (1250) (GMC-8 is an emulsifier)	4.1	7.6	85.37	-0.6	10.1

Table 5: Stabilization of Polypropylene (ICI-H) with α -Tocopherol (a) + Polyhydroxy Compound (b)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a) : (b) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)		Yellowness Index (YI) at Pass (Ps)	
		1st Ps	4th Ps	1st Ps	4th Ps
ATP (250) + Glycerol (250)	1:1 (500)	4.5	8.9	6.4	13.4
ATP (250) + Glycerol (500)	1:2 (750)	4.6	7.3	6.9	14.1
ATP (250) + Glycerol (1000)	1:4 (1250)	4.7	10.0	6.0	13.2
ATP (250) + Ethylene glycol (500)	1:2 (750)	4.8	7.2	6.8	15.3
ATP (250) + Butylene glycol (500)	1:2 (750)	4.4	10.0	7.3	15.1

Table 5: Stabilization of Polypropylene (ICI-H) with α -Tocopherol (a) + Polyhydroxy Compound (b) (continued)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a) : (b) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)		Yellowness Index (YI) at Pass (Ps)	
		1st Ps	4th Ps	1st Ps	4th Ps
ATP (250) + Trimethylolpropane (500)	1:2 (750)	4.8	9.2	6.8	16.8
ATP (250) + Pentaerythritol (500)	1:2 (750)	4.1	8.0	8.9	17.8
ATP (250) + Triisopropanolamine (500)	1:2 (750)	4.0	8.2	6.5	17.9
ATP (250) + Panthenol (500)	1:2 (750)	4.5	7.6	8.4	18.7
ATP (250) + Citric acid (500)	1:2 (750)	4.4	8.7	15.6	23.5

Table 5: Stabilization of Polypropylene (ICI-H) with α -Tocopherol (a) + Polyhydroxy Compound (b) (continued)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a) : (b) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)		Yellowness Index (YI) at Pass (Ps)	
		1st Ps	4th Ps	1st Ps	4th Ps
ATP (250) + Boric acid (500)	1:2 (750)	4.1	9.3	13.1	18.8
ATP (250) + Glycerol monostearate (500)	1:2 (750)	4.6	11.0	8.7	16.0
ATP (250) + Ethylenediamine tetraacetic acid (500)	1:2 (750)	5.0	11.0	13.4	26.5
ATP (250) + Nitrilotriacetic acid (500)	1:2 (750)	4.3	12.0	13.7	28.3

Table 5: Stabilization of Polypropylene (ICI-H) with α -Tocopherol (a) + Polyhydroxy Compound (b) (continued)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a) : (b) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)		Yellowness Index (YI) at Pass (Ps)	
		1st Ps	4th Ps	1st Ps	4th Ps
ATP (250) + MD 10249 (500)	1:2 (750)	5.1	11.0	11.1	25.1
ATP (250) + Naug XL-1 ¹⁰ (500)	1:2 (750)	4.3	11.0	14.0	23.4
ATP (250) + Glycerol (500) + PEG-300 ¹¹ (500) + GMC-8 (1250)	1:2 (750) (PEG-300 + GMC-8 is an emulsifying system)	5.0	10.0	9.1	15.8
ATP (250) + GMC-8 (500)	(comparative; GMC-8 is an emulsifier)	5.0	11.0	10.2	18.5

Table 6: Stabilization of Polypropylene (ICI-K) with α -Tocopherol (a) + P-containing sec. Antioxidant I (b) + Polyhydroxy Compound (c)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a) : (b) : (c) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)		Yellowness Index (YI) at Pass (Ps)	
		1st Ps	4th Ps	1st Ps	4th Ps
ATP (250) + E 398 (1000) + Glycerol (500) + PEG-300 (500) + GMC-8 (1250)	1:4:2 (1750) (PEG-300 + GMC-8 is an emulsifying system)	4.7	6.3	-4.6	2.9
ATP (250) + E 398 (1000) + Glycerol (500)	1:4:2 (1750)	4.4	7.2	-3.1	3.7

Table 6: Stabilization of Polypropylene (ICI-K) with α -Tocopherol (a) + P-containing sec. Antioxidant I (b) + Polyhydroxy Compound (c) (continued)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a) : (b) : (c) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)		Yellowness Index (YI) at Pass (Ps)	
		1st Ps	4th Ps	1st Ps	4th Ps
ATP (100) + E 398 (400) + Glycerol (200) + PEG-300 (200) + GMC-8 (500)	1:4:2 (700) (PEG-300 + GMC-8 is an emulsifying system)	6.4	14.1	-4.0	-1.3
ATP (250) + HP-10 (1000) + Glycerol (500) + PEG-300 (500) + GMC-8 (1250)	1:4:2 (1750) (PEG-300 + GMC-8 is an emulsifying system)	4.0	6.3	-4.3	0.8

Table 6: Stabilization of Polypropylene (ICI-K) with α -Tocopherol (a) + P-containing sec. Antioxidant I (b) + Polyhydroxy Compound (c) (continued)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a) : (b) : (c) (Total ppm)	Melt Flow Index (MFI) at Pass (Ps)		Yellowness Index (YI) at Pass (Ps)	
		1st Ps	4th Ps	1st Ps	4th Ps
ATP (250) + HP-10 (1000) + Glycerol (500)	1:4:2 (1750)	4.1	6.3	-4.0	1.5
ATP (250) + TNPP (1000) + Glycerol (500)	- (comparative)	4.7	9.6	-0.4	4.3

Example 2

The procedure described in Example 1 was in principle repeated, but with a few differences as indicated hereinafter. Before the melt flow index, yellowness index and oven aging determinations were effected, part of the
5 polypropylene having incorporated therein the stabilizing mixtures was subjected to γ -irradiation, as also described in more detail hereinafter.

Starting polypropylene: A ethylene-propylene copolymer, obtained from Rexene Inc., U.S.A. and of a type usually employed in γ -irradiation applications.

10 Extrusion: The twin screw extruder and running conditions were as described previously, with the difference that only one extrusion pass was effected; 0.7 kg; screw speed 15 rpm; output approx. 7.5 kg/h; temperatures: hopper 220°C, zone 1 225°C, zone 2 230°C, zone 3 235°C, melt 230°C.

Procedure: Lace was collected and granulated, and the initial melt flow
15 index and yellowness index were determined as described in Example 1, using the same equipment. After compression moulding as before oven lives (days to embrittlement) were determined using circulating-air ovens at 70°C.

Irradiation: A custom irradiation facility was used, with cobalt-60 as the source of γ -irradiation. The total irradiation dose was 2.5 Mrad, the
20 mean dose rate 2.6 Mrad/h. One set of granule samples was maintained at room temperature, and melt flow index and yellowness index were measured 28 days after irradiation. Other samples were subjected to oven heating at 70°C, and yellowness index determined after 1, 7, 14 and 28 days oven aging. Samples of approx. 10 g weight were oven aged in 30 ml open
25 glass bottles of internal diameter approx. 3 cm. Irradiated compression moulded plaques (approx. 25 cm x 25 cm x 1 mm) were cut up and oven aged at 70°C. The first signs of degradation, in particular surface crazing and a significant change in opacity, were recorded, and embrittlement on bending determined manually.

30 The results of the testing are presented in Table 7 hereinafter.

Table 7: Stabilization of γ -Irradiated Polypropylene copolymer (Rexene) with Tocopherol/6-Chromanol (a) + P-containing sec. Antioxidant I or Polyhydroxy Compound (b) (Total dose of γ -irradiation: 2.5 Mrad; Mean dose rate: 2.6 Mrad/h; aging temp. 70°C)

Stabilizer (ppm)	Weight Ratio of Stabilizer Components (a) : (b) (Total ppm)	Melt Flow Index		Yellowness Index after:			Time to Embrittlement of Plaques (days)
		After 28 days	After γ -irr. and 28 days storage at room temperature	1	7	14 days	
ATP (250) + E 398 (1000)	1:4 (1250)	17.5	130	13.2	13.5	14.8	41
ATP (250) + Glycerol (500)	1:2 (750)	19.6	140	4.9	4.6	8.3	24
None (unstabilized)	- (comparative)	32	220	1.6	0.8	3.6	16
ATP (250)	- (comparative)	19	210	5.9	4.9	8.6	25
ATP (500)	- (comparative)	18	180	15.0	13.1	15.0	33
ATP (1000)	- (comparative)	17	190	24.2	21.2	22.1	41

Legend for Tables 1-7

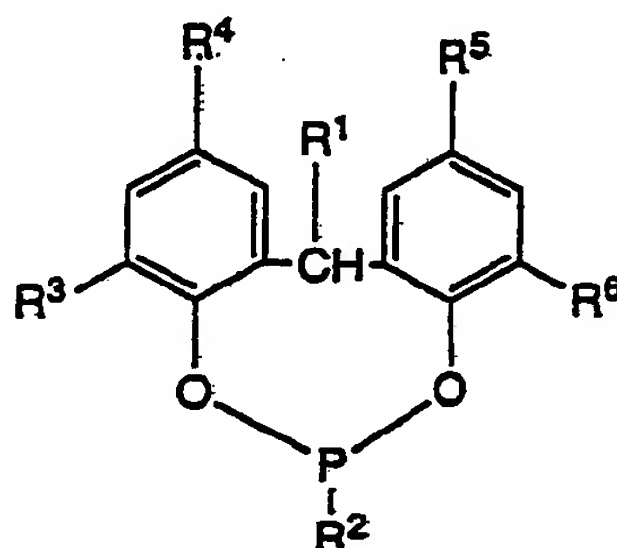
- 1) ATP = dl- α -tocopherol
- 2) E 398 = Ethanox® 398, 2,2'-ethylidene-bis(4,6-di-tert.butylphenyl) fluorophosphonite
- 5 3) TNPP = tris(p-nonylphenyl)phosphite
- 4) GTP = γ -tocopherol
- 5) HP-10 = Mark HP-10, 2,2'-methylene-bis(4,6-di-tert.butylphenyl) octylphosphite
- 6) E 1 = 2,2,5,7,8-pentamethylchroman-6-ol
- 10 7) HMC = 2-hydroxymethyl-2,5,7,8-tetramethylchroman-6-ol
- 8) GMC-8 = Drewmulse® GMC-8, glyceryl(mono)caprylate/caprate
- 9) MD 1024 = Irganox® MD 1024, N,N'-bis[β -(3,5-di-tert.butyl-4-hydroxyphenyl)-propionyl]-hydrazide
- 15 10) Naug. XL-1 = Naugard® XL-1, 2,2'-oxamido-bis[β -(3-(β -(3,5-di-tert.butyl-4-hydroxyphenyl)-propionyloxy))-ethyl]
- 11) PEG-300 = polyethylene glycol

Claims

1. A stabilizing mixture for plastic materials containing polypropylene comprising

(a) a tocopherol or other 6-chromanol compound

5 and (b) a phosphorus-containing secondary antioxidant of the general formula



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wherein

R¹ signifies hydrogen or C₁₋₆-alkyl,

10 R² signifies halogen, C₁₋₁₈-alkyl, C₁₋₁₈-alkoxy or aryloxy

and

R³, R⁴, R⁵ and R⁶, each independently, signify isopropyl or straight- or branched-chain C₄₋₈-alkyl,

wherein the weight ratio of component (a) to component (b) is from about

15 1:0.5 to about 1:20.

2. A stabilizing mixture according to claim 1, wherein the component (a) is α -tocopherol, γ -tocopherol, 2-hydroxymethyl-2,5,7,8-tetramethylchroman-6-ol or 2,2,5,7,8-pentamethylchroman-6-ol.

3. A stabilizing mixture according to claim 1 or 2, wherein the
20 component (b) is 2,2'-ethyldiene-bis(4,6-di-tert.butylphenyl) fluorophosphonite or 2,2'-methylene-bis(4,6-di-tert.butylphenyl) octylphosphite.

4. A stabilizing mixture according to claims 1 to 3, consisting essentially of α -tocopherol as the component (a) and 2,2'-ethyldiene-bis(4,6-di-tert.butylphenyl) fluorophosphonite as the component (b) in a weight ratio
25 (a):(b) of about 1:4.

5. A stabilizing formulation for plastic materials comprising (a) α -tocopherol and (b) one or more polyhydroxy compounds, wherein the weight ratio of component (a) to component (b) is from about 1:0.5 to about 1:4.

6. A stabilizing formulation according to claim 5, wherein the
5 component (b) is one or more of ethylene glycol, butylene glycol, glycerol, trimethylolpropane, pentaerythritol, triisopropanolamine, panthenol, boric acid, glyceryl monostearate and glyceryl(mono)caprylate/caprate.

7. A stabilizing formulation according to claim 5 or 6, characterized in
10 that it is for stabilizing plastic material containing polypropylene and that the weight ratio of component (a) to component (b) is about 1:2.

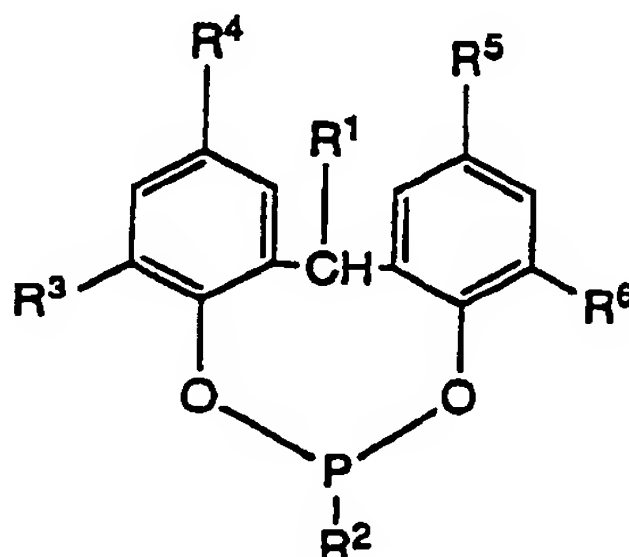
8. A stabilizing formulation for plastic materials comprising (a) α -tocopherol and (b) one or more polyhydroxy compounds, wherein the weight ratio of component (a) to component (b) is from about 1:0.5 to about 1:4, with the exclusion of a stabilizing formulation comprising

- 15 (c) from about 10 to about 50 percent by weight of α -tocopherol;
(d) up to 50 percent by weight of polyethylene glycol and/or
(e) up to 50 percent by weight of glyceryl(mono)caprylate/caprate;
and optionally also (f) up to 20 percent by weight of glycerol,

whereby the total percent by weight of the two, three and four components (c)
20 to (f), as appropriate, amounts to 100.

9. A stabilizing ~~three-component~~ mixture for plastic materials containing polypropylene comprising

- (a) from about 4 to about 50 percent by weight of α -tocopherol,
(b) from about 4 to about 70 percent by weight of a phosphorus-
25 containing secondary antioxidant of the general formula



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wherein

R¹ signifies hydrogen or C₁₋₆-alkyl,

R² signifies halogen, C₁₋₁₈-alkyl, C₁₋₁₈-alkoxy or aryloxy

and

5 R³, R⁴, R⁵ and R⁶, each independently, signify isopropyl or straight- or branched-chain C₄₋₈-alkyl,

and (c) from about 4 to about 70 percent by weight of a polyhydroxy compound,

whereby the total percent by weight of the three components (a), (b) and (c)
10 amounts to 100.

10. A stabilizing three-component mixture according to claim 9, wherein the component (b) is 2,2'-ethylidene-bis(4,6-di-tert.butylphenyl) fluorophosphonite or 2,2'-methylene-bis(4,6-di-tert.butylphenyl) octylphosphite, and the component (c) is one or more of ethylene glycol,
15 butylene glycol, glycerol, trimethylolpropane, pentaerythritol, triisopropanolamine, panthenol, boric acid, glyceryl monostearate and glyceryl(mono)caprylate/caprate.

11. A plastic material containing polypropylene, and any article manufactured therefrom, characterized in that it has been stabilized by
20 incorporation therein of a stabilizing mixture as claimed in any one of claims 1 to 4, or a stabilizing three-component mixture as claimed in claim 9 or 10,

12. A plastic material, and any article manufactured therefrom, characterized in that it has been stabilized by incorporation therein of a
25 stabilizing formulation as claimed in any one of claims 5 to 8.

13. A plastic material or article according to claim 11 or 12 wherein the stabilizing mixture, formulation or three-component mixture is incorporated in a concentration of from about 0.005 to about 1% by weight, about 0.01 to about 1% by weight, or about 0.01 to about 0.25% by weight,
30 respectively, based on the weight of the plastic material.

14. A plastic material containing polypropylene or any article manufactured therefrom, according to any one of claims 11, 12 and 13,

whenever subjected to γ -irradiation at a dose of from about 0.5 to about 5.0 Mrad.

15. A process for producing a stabilizing mixture, stabilizing formulation or stabilizing three-component mixture as claimed in any one of
5 claims 1 to 10 comprising mixing the components (a) and (b), and (c), as appropriate, with each other in the appropriate weight ratio.

16. The use of a stabilizing mixture, formulation or three-component
mixture as claimed in claim 1, 2, 3 or 4, or 5, 6, 7 or 8, or 9 or 10, as
appropriate, for stabilizing a plastic material containing polypropylene, or
10 plastic material.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 92/02572

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08K5/00; //(C08K5/00, C08K5:15, C08K5:5393)		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	PATENT ABSTRACTS OF JAPAN vol. 1, no. 91 (C-77)24 August 1977 & JP,A,52 050 983 (ADEKA ARGAS KAGAKU KK) 21 October 1975 see abstract -----	1
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
01 FEBRUARY 1993	- 5. 02. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	Dieter Schöler	